NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

Technical Report 32-1309

The Effect of Substrate Structure on the Deposition of Evaporated Carbon

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Preface

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Abstract

A carbon deposition effect similar to that reported by Lewis and Floyd, but one that requires a different explanation, was discovered during studies of tensile creep on pyrolytic and glassy carbons.

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I. Introduction

Lewis and Floyd (Ref. 1) have reported the formation of an oriented graphite "skin" on various carbon surfaces heated by RF induction to temperatures $\geq 2600°C$ while in an inert gas and in contact with conventional synthetic graphite. They have interpreted their observations in terms of reorientation of the substrate, induced perhaps by the free energy of the anisotropic surface of graphite. This report describes some observations on a similar carbon deposition effect that require a different explanation.

II. Observations

In the course of tensile creep studies on pyrolytic and glassy (vitreous) carbons, it was found that carbon deposits built up on the exposed gage-section surfaces of the specimens during tests lasting several hours at temperatures in the range of 2700–2900°C. The creep tests were carried out in argon at one atmosphere in a tubular resistance furnace with a single-spiral element of coke-pitch graphite. The equipment and techniques have been described in detail elsewhere (Ref. 2, 3).

The most prominent carbon deposits formed on the layer-plane edge "a" surfaces of pyrolytic-carbon specimens. As shown in Fig. 1, deposition was concentrated near the ends of the gage section, tapering off rapidly toward the center of the specimen and terminating abruptly where the grips (glassy-carbon inserts in coke-pitch graphite bodies) made intimate contact with the specimen. These "a" surface deposits were quite adherent, and differential thermal expansion stresses resulted in kink deformation of the specimen corners and, finally, cracking and flaking of the deposit on cooling to room temperature. The drawing-ink fiducial marks were placed on the specimen before testing. Almost no deposition occurred on the layer-plane face "c" surfaces of the pyrolytic specimens, as can be seen in Fig. 1.

Thin, powdery, poorly adherent deposits formed on the surfaces of the glassy-carbon specimens.

Flakes of the deposit removed from pyrolytic "a" surfaces were examined by X-ray diffraction and found to be well graphitized and randomly oriented. Examination of metallographically polished sections of the deposit in

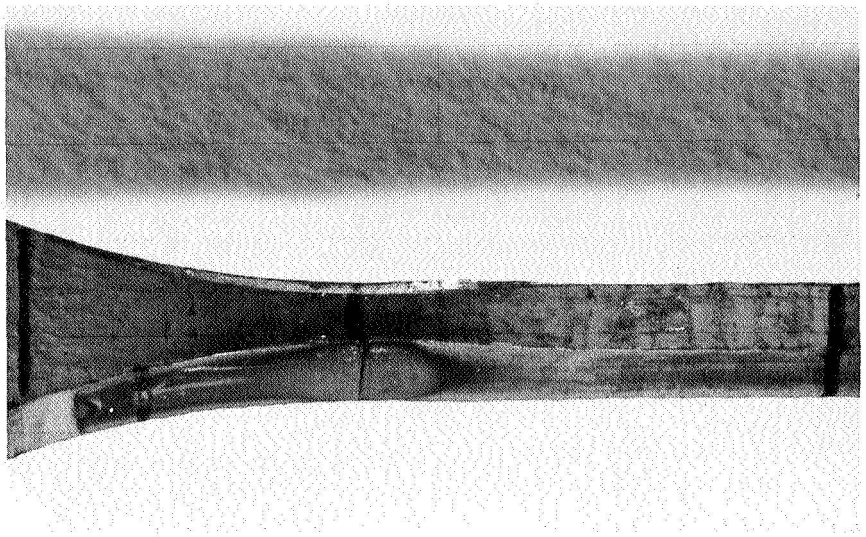

Fig. 1. Carbon deposit on layer-plane edge surface of pyrolytic carbon. Magnification 3×.

polarized light confirmed that the texture was random. As shown in Fig. 2, there was no growth-cone structure, and the particle size was a few microns in diameter.

The source of the deposit was traced to evaporation of carbon from the graphite heating element. By shielding the gage section with a wrapping of flexible graphite foil, deposition on the specimen was greatly reduced. A sheet of foil wrapped snugly around the grips and tied with carbon yarn to completely shield the specimen from the heating element eliminated deposition on the specimen entirely. However, a heavy deposit, which reproduced the spiral geometry of the element, formed on the outer surface of the shield. Examination of the heating element showed extensive loss of material from the edges of the spiral turns. The evaporated carbon evidently originated there and was carried to the specimen partly by flow of argon gas admitted through the viewing ports, and partly by diffusion and convection.

Considerable deposition also occurred on the conventional graphite specimen grips, especially the cooler outer ends, making them difficult to disassemble after prolonged high-temperature creep tests. The distinctive deposition pattern (Fig. 1) can be explained in terms of the distribution of deformation and temperature along the specimen. Continuing plastic strain in the uniform gage section prevented the build up of adherent deposits there; but in the throat regions at each end, the strain fell off rapidly because of the increasing cross section. Near the gripped portion, the specimen was partially shielded by the grip body, reducing somewhat the deposit thickness. Micropyrometer measurements showed a small but definite negative temperature gradient from the center to the ends of the uniform gage section, and the temperature fell rapidly in the grips because of conduction and radiation losses out the ends of the furnace. The heating element was, of course, hotter than the specimen.

III. Conclusions

Two conclusions are drawn from these observations: (1) the deposited carbon was evaporated from the coke-pitch graphite heating element; the carbon did not come from the pyrolytic- or glassy-carbon specimens; (2) the nucleation, growth, and adherence of evaporated carbon films at high temperatures is strongly dependent on the nature of the substrate surface (i.e., deposits form readily on pyrolytic "a" surfaces, while glassy-carbon surfaces are much less effective substrates, and virtually no deposition occurs on pyrolytic "c" faces).

These features are similar to those observed by Lewis and Floyd, and it seems likely that a common explanation should apply. They found deposition to have much the same dependence on substrate surface, and their deposits were also associated with the presence of coke-pitch graphite. The differences in deposit-orientation texture in the two sets of experiments could be a result of differences in the experimental arrangements. In the

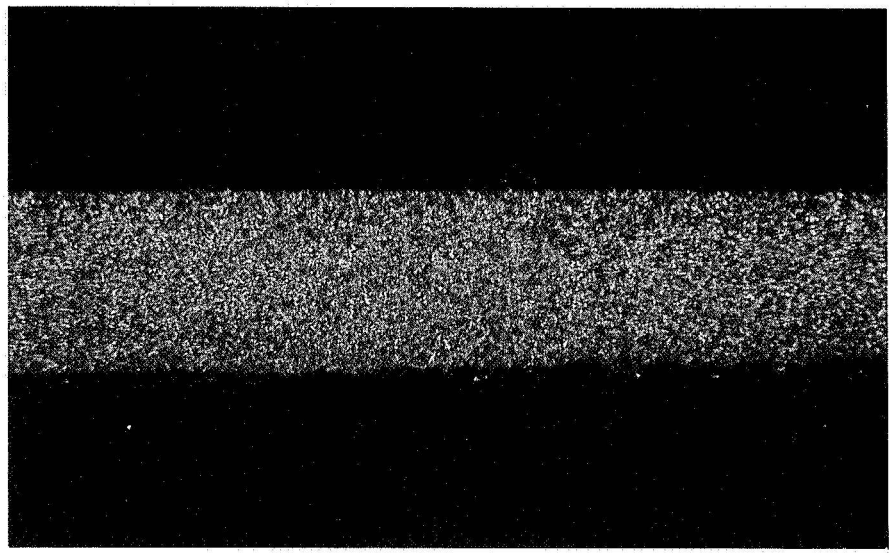

Fig. 2. Cross section of carbon deposit. Polarized light, magnification 200×.

apparatus used by Lewis and Floyd, the distance from the probable source of the evaporated carbon to the substrate on which it was deposited was quite short, in general much less than a centimeter. It is reasonable to suppose that carbon that evaporated as graphitic platelets would deposit in the same form in these circumstances, producing the pyrolytic-type texture they observed. In the present experiments, the distance from source to substrate was several centimeters, allowing aggregation of the carbon into larger soot-like particles before deposition on the specimen surface.

The pyrolytic carbon used here was deposited at 2200°C from methane by a commercial producer (Super Temp). It was well graphitized (interlayer spacing $d \leq 3.36$ Å) and highly oriented (average layer-plane mis-orientation ≤ 2 deg) in the gage and throat regions as a result of the high-temperature tensile deformation. The glassy carbon (Tokai Electrode Co., GC-30) was isotropic and disordered ($d \simeq 3.42$ Å). Consideration of the structural characteristics of these different surfaces suggests that free carbon bonds on the edges of graphitic layer planes may play an important role in the deposition phenomena. Again, the pyrolytic "a" surfaces on which deposition was most pronounced consist entirely of layer-plane edges. On the pyrolytic "c" faces where no deposition occurred, edge atoms are exposed only at imperfections such as cleavage steps. On the glassy-carbon surfaces, a uniform but dilute distribution of edge sites would be expected because of the isotropy and small crystallite size ($\simeq$100 Å), but the number of free bonds might be reduced by the suspected high incidence of cross-link bonding in this type of material. The porosity and structural heterogeneity of the coke-pitch graphite surfaces undoubtedly affected both the evaporation and condensation characteristics of this material. The influence of chemical bonding at exposed layer-plane edge sites on deposit nucleation and adherence could account qualitatively for most of the deposition phenomena reported here, and appears to offer a reasonable alternative to thermodynamically-induced reorientation as an explanation for the observations of Lewis and Floyd.

References

1. Lewis, J. C., and Floyd, I. J., "Reorientation Effects in Vitreous Carbon and Pyrolytic Graphite," *J. Mater. Sci.*, Vol. 1, No. 2, pp. 154–159, May 1966.

2. Kotlensky, W. V., and Martens, H. E., *Tensile Properties of Pyrolytic Graphite to 5000°F*, Technical Report 32-71. Jet Propulsion Laboratory, Pasadena, Calif., March 10, 1961. (Also appears in *High Temperature Materials II*, AIME Met. Soc. Conf., Vol. 18, pp. 403–418. Edited by G. M. Ault, W. F. Barclay, and H. P. Musinger. Interscience Publishers, New York, 1963.)

3. Fischbach, D. B., *Tensile Creep Studies on Glassy Carbon*, Technical Report 32-1228. Jet Propulsion Laboratory, Pasadena, Calif., March 1, 1968.